A MILD, CHEMICAL CONVERSION OF CELLULOSE TO HEXENE AND OTHER LIQUID HYDROCARBON FUELS AND ADDITIVES.

J. Michael Robinson

Chemistry Department, The University of Texas of the Permian Basin
Odessa, TX 79762

Keywords: Biomass, Liquid fuels, Chemical reduction

INTRODUCTION

Biomass fermentations and high temperature and pressure pyrolysis processes that produce gas or liquid fuels are legion. They all have drawbacks. For example, the theoretical limit of ethanol production is 67% due to the loss of 1/3 of the available carbon as carbon dioxide gas during the fermentation. Pyrolytic reactions usually lose carbon as char and gases and may achieve about 80% carbon conversion [1] Furthermore, pyrochemical processes usually require nearly dry feedstocks. Obviously, there remains a need for a variety of fuels from many sources, especially conventional liquid fuels. To resolve this fuel problem and to use a renewable resource, a strategy was selected to prepare valuable hydrocarbons from biomass by a chemical process.

Our initial goal was to develop an efficient multistep chemical process for the conversion of the principle components of biomass, cellulose and hemicellulose, into hydrocarbon fuels. Separation of these components and/or the use of selective reactions might allow for 100% carbon conversion by keeping the carbon chain intact. Furthermore, if initial reactions could be conducted in an aqueous medium, then the use of wet feedstocks would be possible. Overall, a six carbon sugar polymer, cellulose, would afford a single pure hydrocarbon product such as hexene. This is precisely what we have developed, a novel *chemical* process.

RESULTS AND DISCUSSION

Our use of the term *chemical* implies the typical mild conditions usually employed in glass vessels. This process consists of three to four separate reactions, the first two of which occur in water. **Scheme I** comprises a brief summary of the main reaction steps that achieve the strategic objectives of the organic portion of the process. For simplicity in this abstract, Scheme I is shown with cellulose rather than raw biomass, although the latter works as well.

Step 1 is a reductive depolymerization of carbohydrate biopolymers. Cellulose is simultaneously hydrolysed in dilute acid and catalytically hydrogenated to glucitol (commonly named sorbitol) in near quantitative yields.[2] Hemicellulose is similarly converted into xylitol and sorbitol. Lignin, if present, is simply removed by filtration after the reaction. While the acid is mild, the highly selective rutheniun catalyst is only active at the temperature shown. Thus, Step 1 uniquely provides the required polyols required for the next reaction and simultaneously provides a facile separation of lignin.

Step 2 of the process is also a key reaction: the chemical conversion of polyhydric alcohols to liquid hydrocarbons. The major part of all the reduction requirements occurs in this conversion. Reduction of five hydroxyl groups of sorbitol occurs while one hydroxyl group gives substitution.

According to an early reference,[3] sorbitol reacts with aqueous HI and red phosphorous to afford 2-iodohexane in 95% yield. By-product I_2 is consumed by phosphorous.

Our strategy to overcome the physical problems of I_2 phase separation as a solid or of using solid red phosphorous was to use homogeneous chemical agents that concomitantly reduce I_2 to regenerate HI.[4] If the I_2 reacts quickly, it does not interfere with the polyol reduction reaction. Such use met with the unexpected results of simultaneous alkene formation and oligomerization. Considerable effort has been extended toward identifying the various products and the variables that control their formation.

Thus in Step 2, polyhydric alcohols such as sorbitol are reduced essentially quantitatively to a mixture of halocarbon and hydrocarbon compounds by reaction with hydriodic acid (HI) and a phosphorous type reducing agent, either phosphorous acid (H_3PO_3) or hypophosphorous acid (H_3PO_2). The reaction occurs in boiling aqueous solution at atmospheric pressure for about 1-2 hours. Reaction conditions were varied to give on one extreme about 99% 2-iodohexane and on the other extreme about 86% hydrocarbons with the remainder being halocarbons. The immiscible products are simply removed as a separate phase from the water solution. So Step 2 not only provides a highly reduced C_6 compound but also C_{12}, C_{18}, and C_{24} hydrocarbons. These groups represent fuels in the range of gasoline, kerosene, diesel, and fuel oil, respectively. Material balances (yields) are 100%(±4%) and were determined by GC/MS analyses of isolated product.

Each hydrocarbon group is a mixture of alkene isomers. The higher homologues typically contain a ring. An example structure for the $C_{12}H_{22}$ isomers (1,2,4-trimethyl-3-propylcyclohexene, MW = 166) is shown in Scheme I. Halocarbons detected were 2-iodohexane, isomers of $C_6H_{12}I_2$, and traces of $C_{12}H_{22}I_2$. Mannitol and xylitol gave similar results.

In contrast, we found that Step 2 products such as these do not form from glucose; it must first be reduced to sorbitol. Such products do not form on treatment of wood with HI.[5] In fact, these authors found that H_3PO_2 greatly "suppresses the yield of oil products." Products obtained in this manner are complex mixtures of high molecular weight oils and tars containing oxygen and high percents of iodine, not specific molecular weight range small hydrocarbons as in our process.

Step 3 might be considered a cleanup reaction in that all of the remaining halocarbons in mixtures from Step 2 are subsequently converted to alkenes by an elimination reaction with potassium hydroxide (KOH) in boiling alcohol. Vast differences in boiling points of hexene (68 °C) from the other higher mass hydrocarbons, 200 °C and 300 °C, allow facile separation by distillation of the final mixture. The mixture of isomers in each group depresses the melting point and helps the fuel remain liquid.

The elimination of HI (Step 3) by KOH produces KI as insoluble by-product. KI can be recycled to KOH and HI by electrochemical means using Aqua-Tech's bipolar cells.[6] Such regenerations are commercially economical. Hexene distilled after Step 3 is very low in iodine impurity, typically ranging from low teens to near 100 ppm. Further lowering of the iodine content is desired for two reasons: (1) potential corrosion due to the HI produced upon combustion, and (2) potentially expensive iodine replacement costs. However, 35 ppm iodine content only increases the cost of hexene by about $0.002/gal.

There are several optional steps, one of which is shown as **Step 4** in Scheme I. Catalytic hydrogenation of hexene furnishes hexane, an important industrial solvent. Hydrolysis of 2-iodohexane to 2-hexanol is another optional reaction to a value added product.

Physical values, H/C ratio, and octane numbers are shown for these fuels and compared to conventional liquid fuels in Table 1. Hexene, for example, has a RON of 93, density of 0.68, and a H/C ratio of 2, all ideal for gasoline. The C_{12} hydrocarbons have several desirable properties (less volatile, highly branched, cyclic, partially unsaturated, and a H/C ratio of 1.8) that should contribute to a high RON. This group might be suitable as a narrow boiling point range gasoline. However, this C_{12} mixture should have a density of 0.8 and a bp of about 200 °C, similar to the values of kerosene. The C_{18} and C_{24} isomer mixtures likely fit into the diesel and fuel oil ranges. Oxygenates marketed today are also compared with 2-hexanol.

SUMMARY AND ECONOMIC PROJECTION

This multistep *chemical* process for reduction of biomass to liquid hydrocarbon fuels is the first of its kind. It stands in sharp contrast to other research areas that follow classical lines of bio-(fermentation) or thermal (pyrolysis) conversion. In fact, uncoupling the reduction process to a series of mild selective chemical reactions was the key to the problem. As a result, economic advantages abound. One particular advantage of this *chemical* process is that both Step 1 and Step 2 reactions take place in water as solvent, which allows the use of wet biomass. The water immiscible organic products of Step 2 simply coalesce as an upper layer facilitating their separation by mere decantation. Another benefit of the process is that the cyclic alkene dimers and trimers produced directly in Step 2 actually require less reduction, 10% and 13%, respectively, than hexene. These oligomeric hydrocarbons also do not require base treatment and subsequent reagent regeneration costs as do the haloalkanes. Step 2 is highly tunable, which allows a choice of products. Each simple reaction step can be driven to essentially quantitative yield resulting in the same high yield for the entire process.

While we may only use hydrogen in Step 1, and the optional Step 4, it is convenient at this time to estimate the total costs of reduction based on a typical price for hydrogen. Using a hydrogen cost of $0.54/lb and a cost range of $10 to $40/ton for biomass (dry weight basis) containing 75% holocellulose, then total feedstock and reduction costs might be estimated as $0.49 to $0.64 per gallon for hexene. Similarly, the C_{12} and C_{18} isomers range from $0.44 to $0.60/gal. However, there are other chemical and mechanical costs associated with this multiple step process that will definitely contribute to overall process economics. Even if the real costs are twice as much, it might still be economical. Establishment of accurate economics will take some time. Total costs depend upon the exact steps, reagents, products, and precisely how the reagents are recycled. It is possible that the high quality, high value products available *via* this process may indeed be economically attractive in the near future, perhaps as fuel additives, even without a change in the margin of fossil fuels. Thanks to strong financial support from several sources, we are continuing to develop this process.
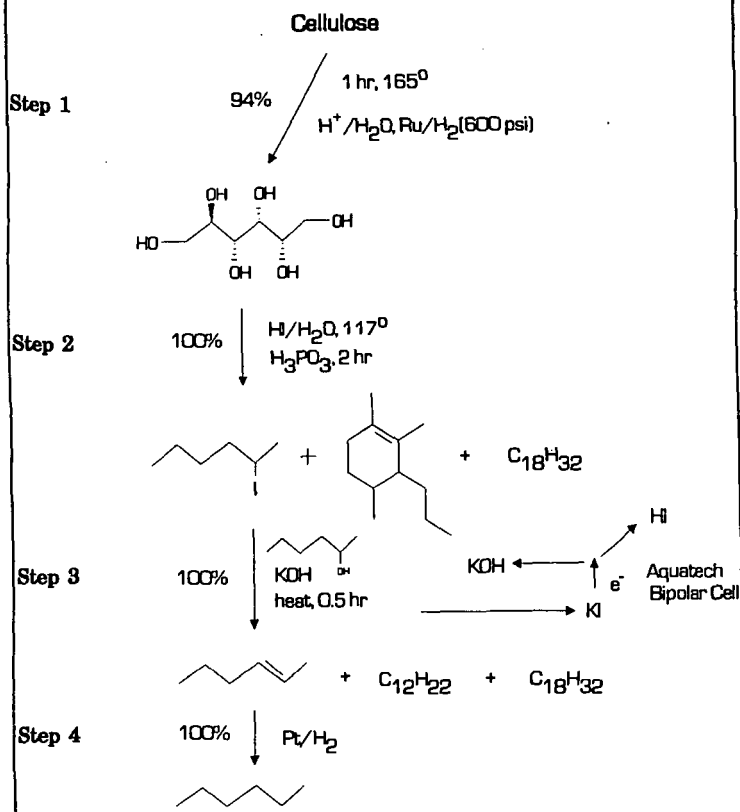
REFERENCES

1. Soltes, E.J. "Of Biomass, Pyrolysis, and Liquids Therefrom", Ch. 1 in ACS Symposium Series #376 "Pyrolysis Oils From Biomass; Producing, Analyzing, and Upgrading" Soltes, E.J. and Milne, T.A., Editors, American Chemical Society, Washington, D.C., **1988**.
2. Sharkov, V.I. "Production of Polyhydric Alcohols from Wood Polysaccharides," *Angew. Chem. I.E.E.* **1963**, *2*, 405.
3. Vincent,C.; Delachanal "Work with Sorbitol" *Compt. Rend*, **1890**, *109*, 677; *Beil.* **1918**, First Work, Band I, System 59, 533.
4. Foster,L.S.; Nahas,H.G.,Jr. "Hydriodic Acid: Regeneration of Oxidized Solutions," *Inorg. Synth.*, Vol. 2, 210, W.C. Fernelius, Ed., **1946**.
5. Cooper,D.; Douglas,M.; Ali,O.; Afrashtehfar,S.; Ng,D.; Cooke,N. "A Low Pressure-Low Temperature Process for the Conversion of Wood to Liquid Fuels and Chemicals Using Hydrogen Iodide" *Canadian Bioenergy R&D Semin. [Proc.] 5th*, **1984**, 455.
6. Mani,K.N. "Electrodialysis Water Splitting Technology," Aquatech Systems Report, Allied Signal, Inc., Warren, NJ, **1990**.

ACKNOWLEDGMENT

Scheme I

Cellulose

Step 1   94%   1 hr, 165°
H^+/H_2O, Ru/H_2(600 psi)

Step 2   100% HI/H_2O, 117°
H_3PO_3, 2 hr

$+$ $+$ $C_{18}H_{32}$

Step 3   100%   KOH heat, 0.5 hr   KOH ←   HI   e⁻   Aquatech Bipolar Cell   KI

$+$ $C_{12}H_{22}$ $+$ $C_{18}H_{32}$

Step 4   100% Pt/H_2

Table 1: Fuel Values

HYDROCARBONS

Compound	Formula	bp °C	RVP	d	H/C	Therm Val	Oct N
Hexane	C6H14	68	35	0.66	2.33	45 MJ/kg	25
Hexene	C6H12	69		0.67	2.0	(44.5)	93
gasoline	C4-C12	27-225	7-8	0.75	2.0	47.3	88
Dimers	C12H22	180-200		(0.76)	1.8		(high)
diesel	C14-C19	240-360	nil	0.84	2.1	43	
Trimers	C18H32	280-300		(0.8)	1.8		

OXYGENATES

Compound	Formula	bp °C	RVP	d	% O	Therm Val	Oct N
Methanol	CH4O	65		0.79	50	22.4 MJ/Kg	106
Ethanol	C2H6O	78	18	0.79	35	29.4	115
MTBE	C5H12O	56	8	0.74	18.2	38	110
ETBE	C6H14O	73	4	0.74	15.7		112
2-Hexanol	C6H14O	136		0.81	15.7	39	(high)